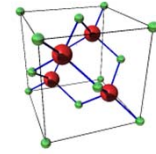


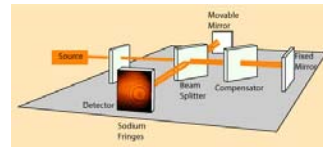
## Phys 446:



# Solid State Physics / Optical Properties

Lattice vibrations:  
Thermal, acoustic, and optical properties

Fall 2015



Lecture 4

Andrei Sirenko, NJIT

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## Solid State Physics

### Lecture 4

Last weeks:

(Ch. 3)

- Diffraction from crystals
- Scattering factors and selection rules for diffraction



Today:

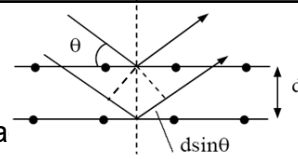
- Lattice vibrations: Thermal, acoustic, and optical properties

This Week:

- Start with crystal lattice vibrations.
- Elastic constants. Elastic waves.
- Simple model of lattice vibrations – linear atomic chain
- HW1 and HW2 discussion

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**Material to be included in the 1<sup>st</sup> QZ**



- Crystalline structures. Diamond structure. Pa  
7 crystal systems and 14 Bravais lattices
- Crystallographic directions  
and Miller indices

$$d_{hkl} = \frac{n}{\left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right)^{1/2}}$$

- Definition of reciprocal lattice vectors:

$$\mathbf{b}_1 = \frac{2\pi}{V} \mathbf{a}_2 \times \mathbf{a}_3, \quad \mathbf{b}_2 = \frac{2\pi}{V} \mathbf{a}_3 \times \mathbf{a}_1, \quad \mathbf{b}_3 = \frac{2\pi}{V} \mathbf{a}_1 \times \mathbf{a}_2$$

- What is Brillouin zone
- Bragg formula:  $2d \cdot \sin\theta = m\lambda$  ;  $\Delta\mathbf{k} = \mathbf{G}$

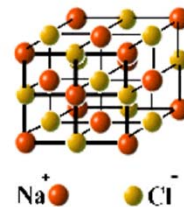
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- Factors affecting the diffraction amplitude:

Atomic scattering factor (form factor):  $f_a = \int n(\mathbf{r}) e^{i\Delta\mathbf{k} \cdot \mathbf{r}} d^3r$   
reflects distribution of electronic cloud.

In case of spherical distribution  $f_a = \int_0^{r_0} 4\pi r^2 n(r) \frac{\sin(\Delta k \cdot r)}{\Delta k \cdot r} dr$

- Structure factor  $F = \sum_j f_{aj} e^{2\pi i(hu_j + kv_j + lw_j)}$



where the summation is over all atoms in unit cell

- Be able to obtain scattering wave vector or frequency from geometry and data for incident beam (x-rays, neutrons or light)

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**Material to be included in the 2<sup>nd</sup> QZ  
TBD**

Elastic stiffness and compliance. Strain and stress: definitions and relation between them in a linear regime (Hooke's law):

$$\sigma_{ij} = \sum_{kl} C_{ijkl} \varepsilon_{kl} \quad \varepsilon_{ij} = \sum_{kl} S_{ijkl} \sigma_{kl}$$

- Elastic wave equation:  $\frac{\partial^2 u}{\partial t^2} = \frac{C_{eff}}{\rho} \frac{\partial^2 u_x}{\partial x^2}$  sound velocity  $v = \sqrt{\frac{C_{eff}}{\rho}}$

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- Lattice vibrations: acoustic and optical branches  
In three-dimensional lattice with  $s$  atoms per unit cell there are  $3s$  phonon branches:  $3$  acoustic,  $3s - 3$  optical

- Phonon - the quantum of lattice vibration.  
Energy  $\hbar\omega$ ; momentum  $\hbar\mathbf{q}$

- Concept of the phonon density of states

- Einstein and Debye models for lattice heat capacity.

Debye temperature  $\theta_D = \frac{\hbar v}{k_B} \left( \frac{6\pi^2 N}{V} \right)^{1/3}$

Low and high temperatures limits of Debye and Einstein models

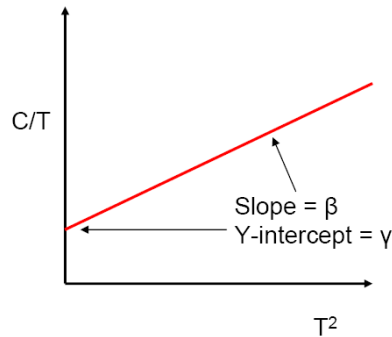
- Formula for thermal conductivity  $K = \frac{1}{3} C v l$

- Be able to obtain scattering wave vector or frequency from geometry and data for incident beam (x-rays, neutrons or light)

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# Crystal Vibrations

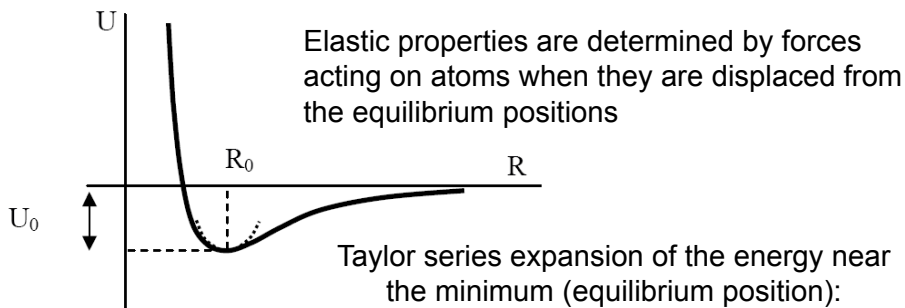
- The study of lattice vibrations is important for understanding how energy is absorbed in solids.
- At low temperatures, most of the energy that is absorbed is of two types: lattice energy, and electronic energy – the heat can go to the electrons, or to vibrations of the positive charges in the lattice.
- We will eventually show that this can be measured with the heat capacity:  $C = dU/dT$
- For a metal,  $C = \gamma T + \beta T^3$ 
  - Electronic term  $\nearrow \gamma T$
  - Lattice term  $\nearrow \beta T^3$



$$C/T = \gamma + \beta T^2$$

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## Elastic properties



$$U(R) = U_0 + \left. \frac{\partial U}{\partial R} \right|_{R_0} (R - R_0) + \frac{1}{2} \left. \frac{\partial^2 U}{\partial R^2} \right|_{R_0} (R - R_0)^2 + \dots$$

For small displacements, neglect higher terms. At equilibrium,  $\left. \frac{\partial U}{\partial R} \right|_{R_0} = 0$

So, 
$$U(R) = U_0 + \frac{ku^2}{2} \quad \text{where} \quad k = \left. \frac{\partial^2 U}{\partial R^2} \right|_{R_0}$$

$u = R - R_0$  - displacement of an atom from equilibrium position <sup>8</sup>

force  $F$  acting on an atom:  $F = -\frac{\partial U}{\partial R} = -ku$

$k$  - interatomic force constant. This is *Hooke's law* in simplest form.

Valid only for small displacements. Characterizes a *linear region* in which the restoring force is linear with respect to the displacement of atoms.

Elastic properties are described by considering a crystal as a homogeneous continuum medium rather than a periodic array of atoms

In a general case the problem is formulated as follows:

- Applied forces are described in terms of *stress*  $\sigma$ ,
- Displacements of atoms are described in terms of *strain*  $\varepsilon$ .
- Elastic constants  $C$  relate stress  $\sigma$  and strain  $\varepsilon$ , so that  $\sigma = C\varepsilon$ .

In a general case of a 3D crystal the stress and the strain are tensors

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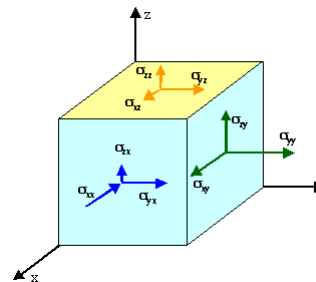
**Stress** has the meaning of local applied "pressure".

Applied force  $\mathbf{F}(F_x, F_y, F_z) \rightarrow$  Stress components  $\sigma_{ij}$  ( $i, j = 1, 2, 3$ )  
 $x \equiv 1, y \equiv 2, z \equiv 3$

General case for stress: *i.e.*  $\sigma_{ij}$

$$F_j = \frac{\partial \sigma_{ij}}{\partial x_j}$$

$$\int_V F_i dV = \int_V \frac{\partial \sigma_{ij}}{\partial x_j} dV = \int_S \sigma_{ij} dS_j$$



Shear forces must come in pairs:  $\sigma_{ij} = \sigma_{ji}$  (no angular acceleration)

$\Rightarrow$  *stress tensor is diagonal, generally has 6 components*

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**Stress** has the meaning of local applied “pressure”.

Applied force  $\mathbf{F}(F_x, F_y, F_z) \rightarrow$  Stress components  $\sigma_{ij}$  ( $i, j = 1, 2, 3$ )

General case for stress: i.e.  $\sigma_{ij}$   $F_j = \frac{\partial \sigma_{ij}}{\partial x_j}$   $x \equiv 1, y \equiv 2, z \equiv 3$

Hydrostatic pressure – stress tensor is equivalent to a scalar: i.e.  $\sigma_{xx} = \sigma_{yy} = \sigma_{zz}$

$$\hat{\sigma} \equiv [\sigma_{ij}] = \begin{bmatrix} -p & 0 & 0 \\ 0 & -p & 0 \\ 0 & 0 & -p \end{bmatrix}$$

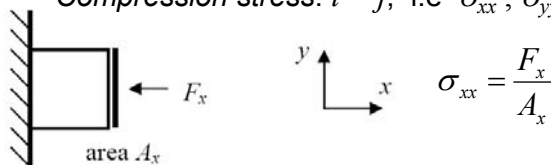
**Stress tensor is a “field tensor” that can have any symmetry not related to the crystal symmetry. Stress tensor can change the crystal symmetry**

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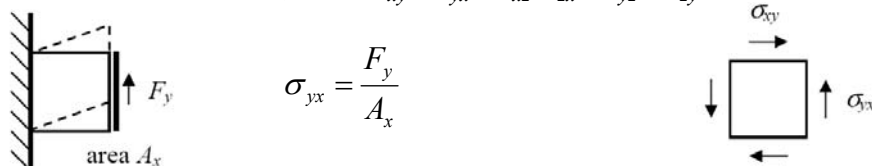
**Stress** has the meaning of local applied “pressure”.

Applied force  $\mathbf{F}(F_x, F_y, F_z) \rightarrow$  Stress components  $\sigma_{ij}$  ( $i, j = 1, 2, 3$ )

Compression stress:  $i = j$ , i.e.  $\sigma_{xx}, \sigma_{yy}, \sigma_{zz}$



Shear stress:  $i \neq j$ , i.e.  $\sigma_{xy}, \sigma_{yx}, \sigma_{xz}, \sigma_{zx}, \sigma_{yz}, \sigma_{zy}$



Shear forces must come in pairs:  $\sigma_{ij} = \sigma_{ji}$  (no angular acceleration)

$\Rightarrow$  stress tensor is diagonal, generally has 6 components <sup>12</sup>

**Strain tensor**  
3x3

$$\varepsilon_{ij} = \frac{\partial u_i}{\partial x_j}$$

In 3D case, introduce the displacement vector as

$$\mathbf{u} = u_x \mathbf{x} + u_y \mathbf{y} + u_z \mathbf{z}$$

Strain tensor components are defined as

$$\hat{\varepsilon} \equiv [\varepsilon_{ij}] = \begin{bmatrix} \varepsilon_{xx} & 0 & 0 \\ 0 & \varepsilon_{yy} & 0 \\ 0 & 0 & \varepsilon_{zz} \end{bmatrix}$$

$$\varepsilon_{xx} = \frac{\partial u_x}{\partial x}$$

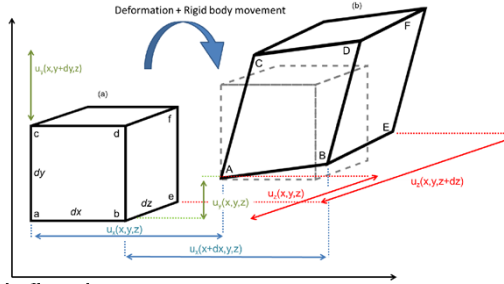
$$\varepsilon_{xy} = \frac{\partial u_x}{\partial y}$$

$$\frac{\Delta V' - dV}{dV} = \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz} = \text{Tr}(\hat{\varepsilon})$$

Share deformations:

$$\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz} = \text{Tr}(\hat{\varepsilon}) = 0$$

$\hat{\varepsilon}$  Can be diagonalized in x-y-z coordinates at a certain point of space  
In other points the tensor is not necessarily diagonal



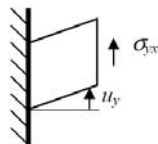
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Strain tensor components are defined as

$$\varepsilon_{ij} = \frac{\partial u_i}{\partial x_j}$$

Compression strain ( $\varepsilon_{xx}$   $\varepsilon_{yy}$   $\varepsilon_{zz}$ ):  $\varepsilon_{xx} = \frac{\partial u_x}{\partial x}$

Shear strain ( $\varepsilon_{xy}$   $\varepsilon_{yx}$   $\varepsilon_{xz}$   $\varepsilon_{zx}$   $\varepsilon_{yz}$   $\varepsilon_{zy}$ ):  $\varepsilon_{xy} = \frac{\partial u_x}{\partial y}$



Since  $\sigma_{ij}$  and  $\sigma_{ji}$  always applied together, we can define shear strains symmetrically:

$$\varepsilon_{ij} = \varepsilon_{ji} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right)$$

So, the **strain tensor is also diagonal** and has 6 components

### Elastic stiffness (C) and compliance (S) constants

relate the strain and the stress in a linear fashion:

$$\sigma_{ij} = \sum_{kl} C_{ijkl} \varepsilon_{kl}$$

This is a general form of the Hooke's law.

$$\varepsilon_{ij} = \sum_{kl} S_{ijkl} \sigma_{kl}$$

6 components  $\sigma_{ij}$ , 6  $\varepsilon_{ij} \rightarrow 36$  elastic constants

Notations:  $C_{mn}$  where 1 = xx, 2 = yy, 3 = zz, 4 = yz, 5 = zx, 6 = xy

For example,  $C_{11} = C_{xxxx}$ ,  $C_{12} = C_{xyxy}$ ,  $C_{44} = C_{yzyz}$

Therefore, the general form of the Hooke's law is given by

$$\begin{pmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{yz} \\ \sigma_{zx} \\ \sigma_{xy} \end{pmatrix} = \begin{pmatrix} \begin{matrix} C_{11} & C_{12} & C_{13} \\ C_{21} & C_{22} & C_{23} \\ C_{31} & C_{32} & C_{33} \end{matrix} & \begin{matrix} C_{14} & C_{15} & C_{16} \\ C_{24} & C_{25} & C_{26} \\ C_{34} & C_{35} & C_{36} \end{matrix} \\ \begin{matrix} C_{41} & C_{42} & C_{43} \\ C_{51} & C_{52} & C_{53} \\ C_{61} & C_{62} & C_{63} \end{matrix} & \begin{matrix} C_{44} & C_{45} & C_{46} \\ C_{54} & C_{55} & C_{56} \\ C_{64} & C_{65} & C_{66} \end{matrix} \end{pmatrix} \begin{pmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ \varepsilon_{zz} \\ \varepsilon_{yz} \\ \varepsilon_{zx} \\ \varepsilon_{xy} \end{pmatrix}$$

compression
mixed
compression
shear
strain

stress
mixed
shear
strain

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### Elastic constants in cubic crystals

Due to the symmetry ( $x$ ,  $y$ , and  $z$  axes are equivalent)  $C_{11} = C_{22} = C_{33}$  ;

$C_{12} = C_{21} = C_{13} = C_{31} = C_{23} = C_{32}$  ;  $C_{44} = C_{55} = C_{66}$

Also, the off diagonal shear components are zero:

$C_{45} = C_{54} = C_{46} = C_{64} = C_{56} = C_{65}$

and mixed compression/shear coupling does not occur:

$C_{45} = C_{54} = C_{46} = C_{64} = C_{56} = C_{65}$

$\Rightarrow$  the cubic elastic stiffness tensor has the form:

$$\begin{pmatrix} C_{11} & C_{12} & C_{12} & & & \\ C_{12} & C_{11} & C_{12} & & & \\ C_{12} & C_{12} & C_{11} & & & \\ & & & C_{44} & 0 & 0 \\ & & & 0 & C_{44} & 0 \\ & & & 0 & 0 & C_{44} \end{pmatrix}$$

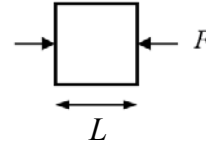
only 3 independent constants



## Elastic constants in cubic crystals

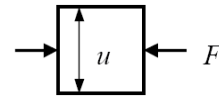
Longitudinal compression  
(Young's modulus):

$$C_{11} = \frac{\sigma_{xx}}{\varepsilon_{xx}} = \frac{F/A}{u/L}$$



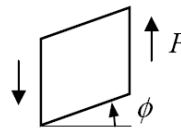
Transverse expansion:

$$C_{12} = \frac{\sigma_{xx}}{\varepsilon_{yy}}$$



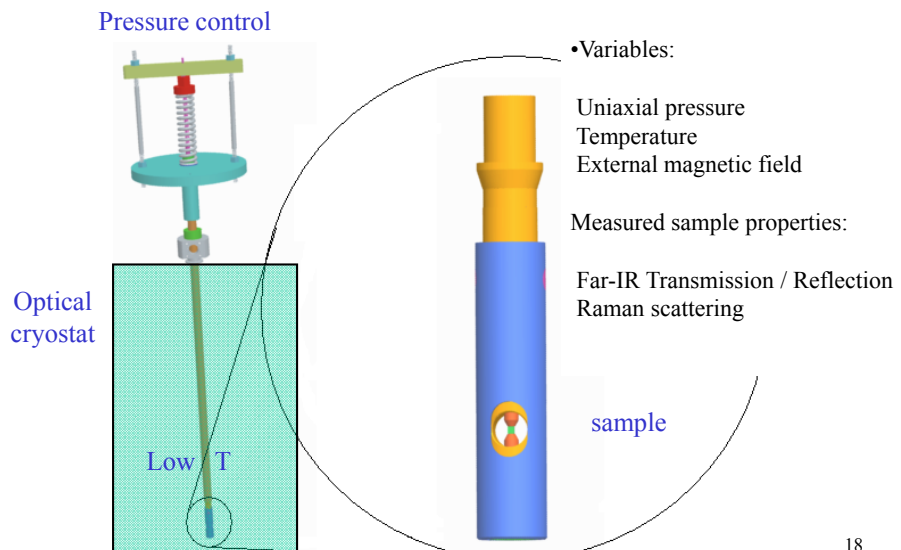
Shear modulus:

$$C_{44} = \frac{\sigma_{xy}}{\varepsilon_{xy}} = \frac{F/A}{\phi}$$



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## Uniaxial pressure setup for optical characterization of correlated oxides



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## Elastic waves

Considering lattice vibrations three major approximations are made:

- atomic displacements are small:  $u \ll a$ , where  $a$  is a lattice parameter
- forces acting on atoms are assumed to be *harmonic*, i.e. proportional to the displacements:  $F = -Cu$  (same approximation used to describe a harmonic oscillator)
- adiabatic approximation is valid – electrons follow atoms, so that the nature of bond is not affected by vibrations

The discreteness of the lattice must be taken into account

For long waves  $\lambda \gg a$ , one may disregard the atomic nature – solid is treated as a continuous medium.

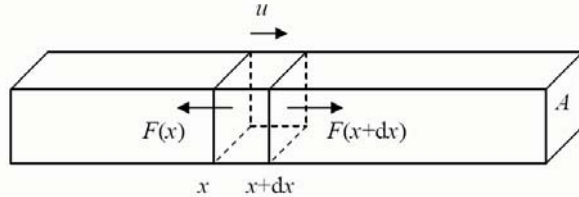
Such vibrations are referred to as *elastic (or acoustic) waves*.

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## Elastic waves

First, consider a *longitudinal wave* of compression/expansion

mass density  $\rho$   
segment of width  $dx$  at the point  $x$ ;  
elastic displacement  $u$



$$m \frac{d^2 u}{dt^2} = \sum F \rightarrow (\rho A dx) \frac{d^2 u}{dt^2} = F(x+dx) - F(x)$$

$$\Rightarrow \rho \frac{\partial^2 u}{\partial t^2} = \frac{1}{A} \frac{\partial F}{\partial x} = \frac{\partial \sigma_{xx}}{\partial x} \quad \text{where } F/A = \sigma_{xx} \quad c_{11} = \frac{\sigma_{xx}}{\epsilon_{xx}} = \frac{F/A}{u/L} \rightarrow \begin{array}{c} \square \\ \leftarrow L \end{array} \leftarrow F$$

Assuming that the wave propagates along the [100] direction, can write the Hooke's law in the form  $\sigma_{xx} = C_{11} \epsilon_{xx}$

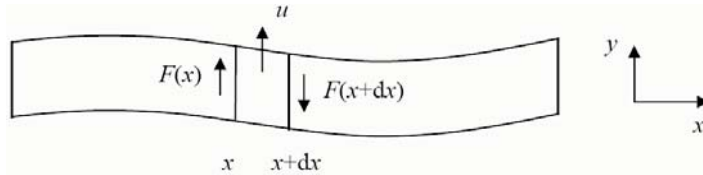
Since  $\epsilon_{xx} = \frac{\partial u_x}{\partial x}$  get **wave equation**:  $\frac{\partial^2 u}{\partial t^2} = \frac{C_{11}}{\rho} \frac{\partial^2 u_x}{\partial x^2}$  20

A solution of the wave equation - *longitudinal plane wave*

$$u(x,t) = Ae^{i(qx-\omega t)} \quad \text{where } q \text{ - wave vector; frequency } \omega = v_L q$$

$$v_L = \sqrt{\frac{C_{11}}{\rho}} \quad \text{- longitudinal sound velocity}$$

Now consider a *transverse wave* which is controlled by shear stress and strain:



In this case

$$\rho \frac{\partial^2 u}{\partial t^2} = \frac{\partial \sigma_{xy}}{\partial x} \quad \text{where } \sigma_{xy} = C_{44} \varepsilon_{xy} \quad \text{and} \quad \varepsilon_{xy} = \frac{\partial u}{\partial x}$$

⇒ wave equation is  $\frac{\partial^2 u}{\partial t^2} = \frac{C_{44}}{\rho} \frac{\partial^2 u}{\partial x^2}$   $v_T = \sqrt{\frac{C_{44}}{\rho}}$  - *transverse sound velocity*

Two independent transverse modes: displacements along  $y$  and  $z$

For  $q$  in the [100] direction in cubic crystals, by symmetry the velocities of these modes are the same - modes are *degenerate*

Normally  $C_{11} > C_{44} \Rightarrow v_L > v_T$

We considered wave along [100].

In other directions, the sound velocity depends on combinations of elastic constants:

$$v = \sqrt{\frac{C_{eff}}{\rho}}$$

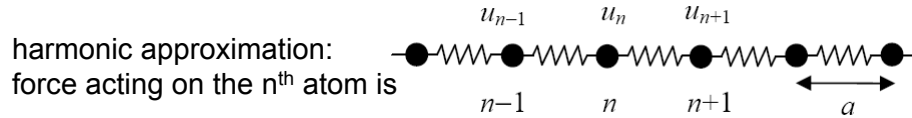
$C_{eff}$  - an effective elastic constant. For cubic crystals:

| Mode           | $\mathbf{q} \parallel [100]$ | $\mathbf{q} \parallel [110]$         | $\mathbf{q} \parallel [111]$          |
|----------------|------------------------------|--------------------------------------|---------------------------------------|
| L              | $C_{11}$                     | $\frac{1}{2}(C_{11}+C_{12}+2C_{44})$ | $\frac{1}{3}(C_{11}+2C_{12}+4C_{44})$ |
| T <sub>1</sub> | $C_{44}$                     | $C_{44}$                             | $\frac{1}{3}(C_{11}-C_{12}+C_{44})$   |
| T <sub>2</sub> | $C_{44}$                     | $\frac{1}{2}(C_{11}-C_{12})$         | $\frac{1}{3}(C_{11}-C_{12}+C_{44})$   |

Relation between  $\omega$  and  $q$  - *dispersion relation*. For sound  $\omega = vq$

## Model of lattice vibrations

one-dimensional lattice: linear chain of atoms



$$F_n = C(u_{n+1} - u_n) + C(u_{n-1} - u_n)$$

equation of motion (nearest neighbors interaction only):

$$M \frac{\partial^2 u}{\partial t^2} = F_n = C(u_{n+1} - u_n) + C(u_{n-1} - u_n) = -C(2u_n - u_{n+1} - u_{n-1})$$

$M$  is the atomic mass,  $C$  – force constant

Now look for a solution of the form  $u(x, t) = Ae^{i(qx_n - \omega t)}$

where  $x_n$  is the equilibrium position of the  $n$ -th atom  $\rightarrow x_n = na$

obtain  $M(-\omega^2)e^{iqna} = -C[2e^{iqna} - e^{iq(n+1)a} - e^{iq(n-1)a}]$  23

$$M(-\omega^2)e^{iqna} = -C[2e^{iqna} - e^{iq(n+1)a} - e^{iq(n-1)a}] \rightarrow$$

$$M\omega^2 = C(2 - e^{iqa} - e^{-iqa}) = 2C(1 - \cos qa) = 4C \sin^2 \frac{qa}{2}$$

$\Rightarrow$  the dispersion relation is  $\omega = \sqrt{\frac{4C}{M}} \left| \sin \frac{qa}{2} \right|$

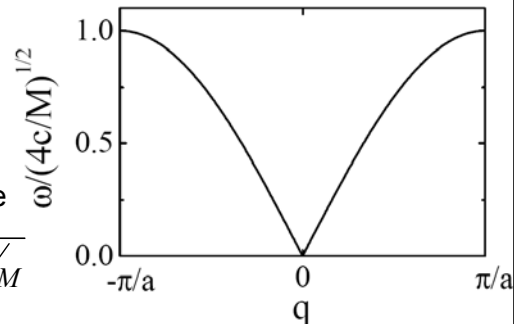
Note: we change  $q \rightarrow q + 2\pi/a$  the atomic displacements and frequency  $\omega$  do not change  $\Rightarrow$  these solutions are physically identical

$\Rightarrow$  can consider only

$$-\frac{\pi}{a} \leq q \leq \frac{\pi}{a}$$

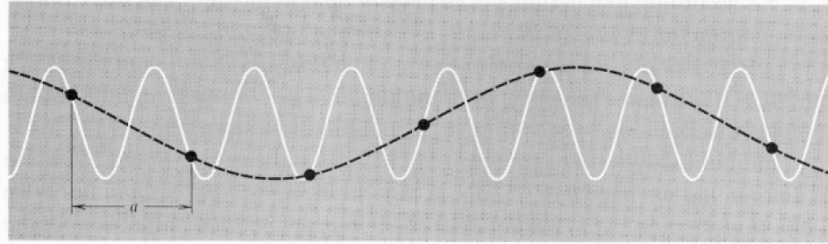
i.e.  $q$  within the first Brillouin zone

The maximum frequency is  $2\sqrt{C/M}$



# Dispersion relation

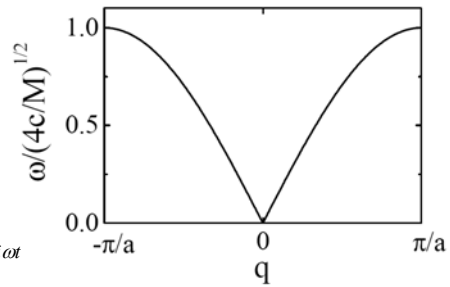
- Another way of showing this, physically, is by looking at the wavelengths of vibration:



- The wave represented by the solid curve conveys no new information not given by the dashed curve. Only wavelengths longer than  $2a$  are needed to represent the motion. This means that  $K$  is limited by  $-\pi/a \leq K \leq \pi/a$

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$$\omega = \sqrt{\frac{4C}{M}} \left| \sin \frac{qa}{2} \right|$$



At the boundaries of the Brillouin zone  $q = \pm\pi/a \rightarrow u_n = A(-1)^n e^{-i\omega t}$   
standing wave

### Phase and group velocity

phase velocity is defined as  $v_p = \frac{\omega}{q}$

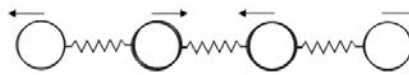
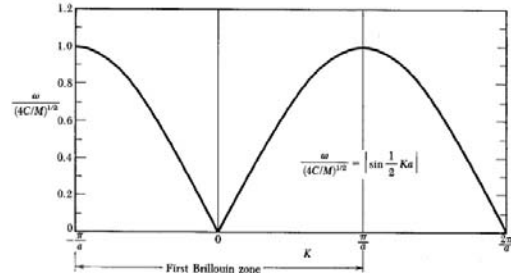
$$\text{group velocity } v_g = \frac{d\omega}{dq} \qquad v_g = a \sqrt{\frac{C}{M}} \cos \frac{qa}{2}$$

$v_g = 0$  at the boundaries of the Brillouin zone ( $q = \pm\pi/a$ )  $\Rightarrow$   
no energy transfer – standing wave

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# Features of the Dispersion Relation

- Most of the waves described by the wavevector  $K$  are travelling waves (meaning that the waves propagate through the lattice).
- However, at the zone boundary, which is  $K = \pm \pi/a$  the wave becomes a standing wave. This means that the wave itself moves neither to the left or two the right.
- It is also a standing wave at  $K = 0$  (the wavelength is infinite)



(at  $Ka = \pm \pi$  these are vibrating out of phase, and so the wave does not propagate)

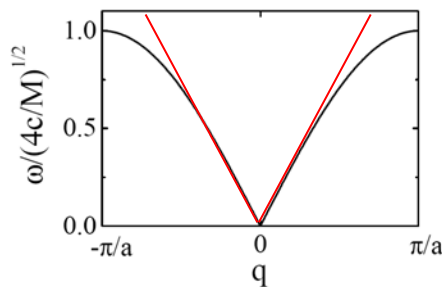
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*Long wavelength limit:  $\lambda \gg a$  ;  $q = 2\pi/\lambda \ll 2\pi/a \Rightarrow qa \ll 1$*

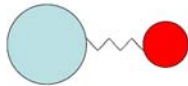
small  $q$  - close to the center of Brillouin zone

$$\omega = \sqrt{\frac{4C}{M}} \left| \sin \frac{qa}{2} \right| \approx \sqrt{\frac{C}{M}} qa \quad - \text{linear dispersion}$$

$$v_p = v_g = a \sqrt{\frac{C}{M}} \quad - \text{sound velocity for the one dimensional lattice}$$

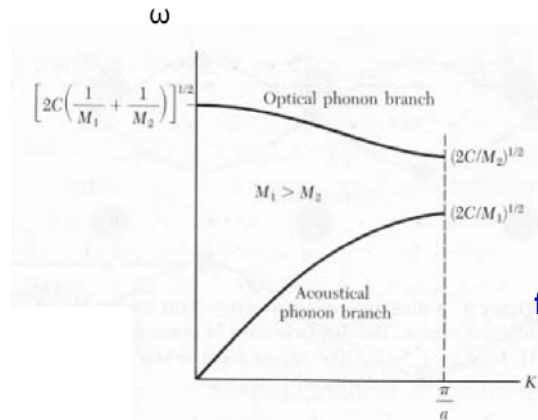
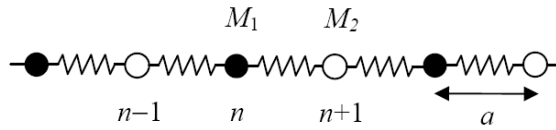


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### Diatomic lattice

one-dimensional linear chain, atoms of two types:  $M_1$  and  $M_2$



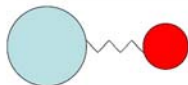
**Optical Phonons can interact with light**

**For diamond Optical phonon frequency is  $\approx 1300 \text{ cm}^{-1}$**

$$\lambda \approx 7700 \text{ nm}$$

(far-IR)

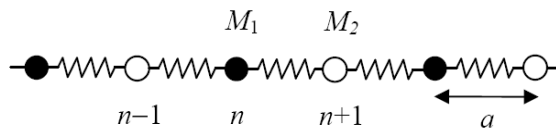
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### Model of diatomic lattice

one-dimensional linear chain, atoms of two types:  $M_1$  and  $M_2$

Treat in similar way, but need two equations of motion:



$$M_1 \frac{d^2 u_n}{dt^2} = -C(2u_n - u_{n+1} - u_{n-1})$$

$$M_2 \frac{d^2 u_{n+1}}{dt^2} = -C(2u_{n+1} - u_{n+2} - u_n)$$

Again, look for a solution of the form  $u_n = A_1 e^{i(qna - \omega t)}$

$$u_{n+1} = A_2 e^{i(q(n+1)a - \omega t)}$$

Substitute this solution into equations of motion

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get system of two linear equations for the unknowns  $A_1$  and  $A_2$

In matrix form: 
$$\begin{bmatrix} 2C - M_1\omega^2 & -2C \cos qa \\ -2C \cos qa & 2C - M_2\omega^2 \end{bmatrix} \begin{bmatrix} A_1 \\ A_2 \end{bmatrix} = 0$$

determinant of the matrix must be zero  $\Rightarrow$

$$(2C - M_1\omega^2)(2C - M_2\omega^2) - 4C^2 \cos^2 qa = 0$$

Solve this quadratic equation, get dispersion relation:

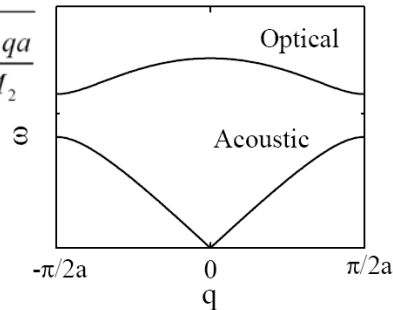
$$\omega^2 = C \left( \frac{1}{M_1} + \frac{1}{M_2} \right) \pm C \sqrt{\left( \frac{1}{M_1} + \frac{1}{M_2} \right)^2 - \frac{4 \sin^2 qa}{M_1 M_2}}$$

Depending on sign in this formula there are two different solutions corresponding to two different dispersion curves

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$$\omega^2 = C \left( \frac{1}{M_1} + \frac{1}{M_2} \right) \pm C \sqrt{\left( \frac{1}{M_1} + \frac{1}{M_2} \right)^2 - \frac{4 \sin^2 qa}{M_1 M_2}}$$

Note: the first Brillouin zone is now from  $-\pi/2a$  to  $+\pi/2a$



The lower curve - *acoustic branch*, the upper curve - *optical branch*.

at  $q = 0$  for acoustic branch  $\omega_0 = 0$ ;  $A_1 = A_2$

$\Rightarrow$  the two atoms in the cell have the same amplitude and the phase dispersion is linear for small  $q$

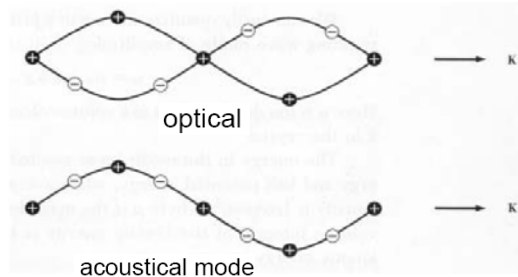
for optical branch at  $q = 0$  
$$\omega_0 = \sqrt{2C \left( \frac{1}{M_1} + \frac{1}{M_2} \right)} \quad M_1 A_1 + M_2 A_2 = 0$$

$\Rightarrow$  the center of mass of the atoms remains fixed. The two atoms move out of phase. Frequency is in infrared – that's why called optical

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## Transverse optical and acoustical modes

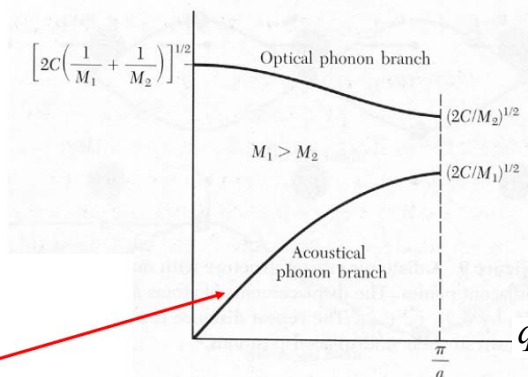


- The acoustic branch has this name because it gives rise to long wavelength vibrations – speed of sound
- The optical branch is a higher energy vibration (the frequency is higher, and you need a certain amount of energy to excite this mode). The term “optical” comes from how these were discovered – notice that if atom 1 is +ve and atom 2 is -ve, that the charges are moving in opposite directions. You can excite these modes with electromagnetic radiation (ie. The oscillating electric fields generated by EM radiation)

## Acoustic/optical branch

$$\omega^2 \cong 2C \left[ \frac{1}{M_1} + \frac{1}{M_2} \right] \quad (\text{optical})$$

$$\omega^2 \cong \frac{1}{2} \frac{C}{M_1 + M_2} q^2 a^2 \quad (\text{acoustic})$$



Acoustic mode is linear in this region, just like the one atom basis lattice

## Zone boundary

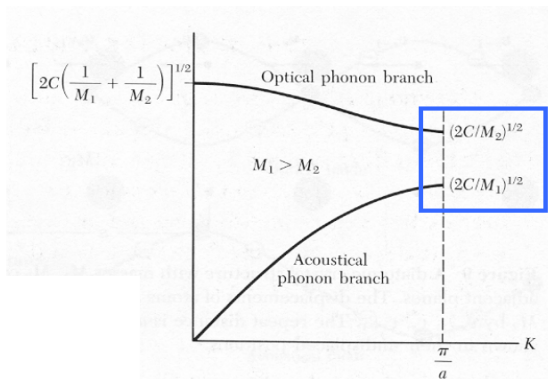
- At the zone boundary,  $Ka = \pm \pi$ , so  $\cos(Ka) = -1$
- Substitute this back into our original equation:

$$\omega^2 = \frac{2C(M_1 + M_2)}{2M_1M_2} \pm \sqrt{\frac{(2C(M_1 + M_2))^2 - 4M_1M_2(-4C^2)}{2M_1M_2}}$$

Roots:

$$\omega^2 \cong \frac{2C}{M_1}$$

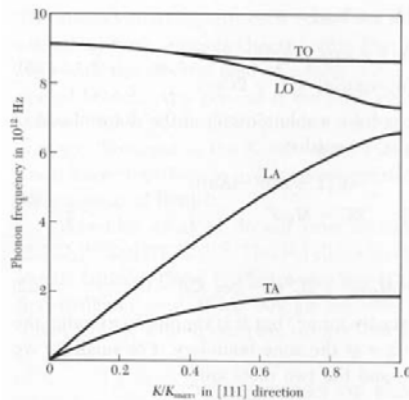
$$\omega^2 \cong \frac{2C}{M_2}$$



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## Two Atoms/Primitive Basis

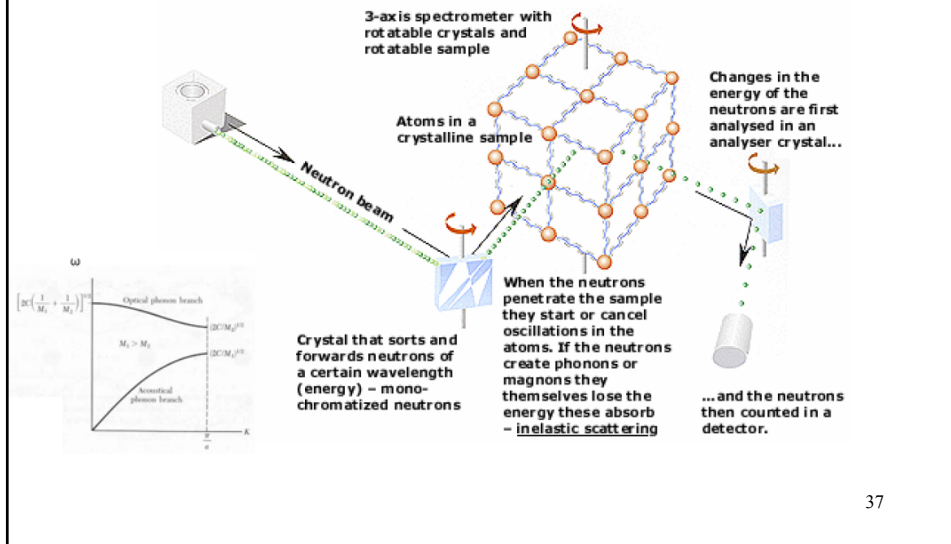
- If there are  $p$  atoms in the unit cell, there has to be  $3p$  branches in the dispersion relation: 3 acoustical branches, and  $3p-3$  optical branches (there are more ways for the atoms to move for the optical modes)
- So, for Germanium, which has 2 atoms/unit cell (diamond structure:  $000$  and  $\frac{1}{4} \frac{1}{4} \frac{1}{4}$ ), there has to be 6 branches: one longitudinal acoustic (LA), 2 transverse acoustic (TA), one longitudinal optical (LO), 2 transverse optical (TO)



(phonon dispersion curve in the  $[111]$  direction for Germanium at 80 K, as determined by inelastic neutron scattering)

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- How do we measure dispersion curves? Inelastic neutron scattering
- If you can measure the energy lost by the neutron (by causing a vibration in the solid), and you can measure which direction you created the wave (the wavevector), then you can construct a dispersion curve



### Summary

- ❖ Elastic properties – crystal is considered as continuous anisotropic medium
- ❖ Elastic stiffness and compliance tensors relate the strain and the stress in a linear region (small displacements, harmonic potential)

Hooke's law:  $\sigma_{ij} = \sum_{kl} C_{ijkl} \epsilon_{kl}$        $\epsilon_{ij} = \sum_{kl} S_{ijkl} \sigma_{kl}$

- ❖ Elastic waves  $\frac{\partial^2 u}{\partial t^2} = \frac{C_{eff}}{\rho} \frac{\partial^2 u_x}{\partial x^2}$  sound velocity  $v = \sqrt{\frac{C_{eff}}{\rho}}$

- ❖ Model of one-dimensional lattice: linear chain of atoms
- ❖ More than one atom in a unit cell – acoustic and optical branches
- ❖ All crystal vibrational waves can be described by wave vectors within the first Brillouin zone in reciprocal space

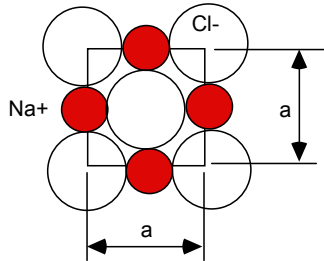
What do we need? 3D case consideration

Phonons. Density of states

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# HW1

Compute the theoretical density of NaCl based on its crystal structure.



For NaCl structure, the crystal lattice parameter is  $a = 2(r_{\text{Na}^+} + r_{\text{Cl}^-})$ , where  $r$  is ionic radius.

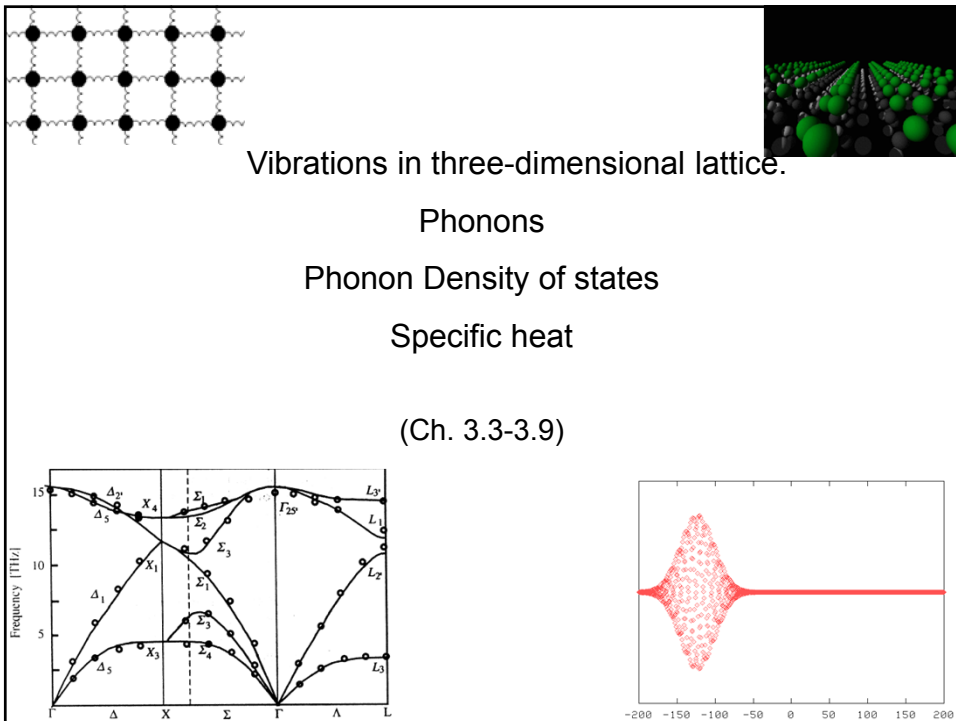
$$\rho = \frac{M}{V} = \frac{4(A_{\text{Na}} + A_{\text{Cl}})}{a^3 N_A}$$

$$= \frac{4 \text{ ions } (22.99 + 35.45) \text{ g/mol}}{2[(0.102 \times 10^{-7} + 0.181 \times 10^{-7}) \text{ cm}]^3 (6.023 \times 10^{23}) \text{ ions/mol}}$$

$$= 2.14 \text{ g/cm}^3 \leftarrow$$

(actual = 2.16 g/cm<sup>3</sup>)

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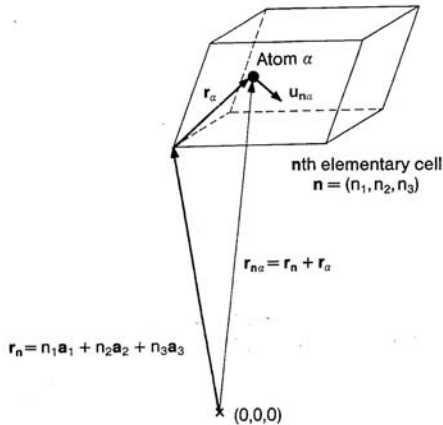


### Three-dimensional lattice

In simplest 1D case with only nearest-neighbor interactions we had  
equation of motion solution

$$M \frac{\partial^2 u}{\partial t^2} = F_n = C(u_{n+1} - u_n) + C(u_{n-1} - u_n) \quad u(x, t) = A e^{i(qx_n - \omega t)}$$

In general 3D case the equations of motion are:



$$M_\alpha \frac{\partial^2 \mathbf{u}_{n\alpha}}{\partial t^2} = \sum_{\mathbf{m}, \beta} F_{n\alpha}^{\mathbf{m}\beta}$$

*N* unit cells, *s* atoms in each →  
3*N*'s equations

Fortunately, have 3D periodicity ⇒  
Forces depend only on difference **m-n**

Write displacements as

$$u_{n\alpha i}(x, t) = \frac{1}{\sqrt{M_\alpha}} u_{\alpha i}(\mathbf{q}) e^{i(\mathbf{q} \cdot \mathbf{r}_n - \omega t)} \quad 41$$

substitute into equation of motion, get

$$-\omega^2 u_{\alpha i}(\mathbf{q}) - \sum_{\beta, j} \sum_{\mathbf{m}} \underbrace{\frac{1}{\sqrt{M_\alpha M_\beta}} F_{n\alpha}^{\mathbf{m}\beta j} e^{i\mathbf{q} \cdot (\mathbf{r}_m - \mathbf{r}_n)}}_{D_{\alpha i}^{\beta j}(\mathbf{q}) \text{ - dynamical matrix}} u_{\beta j}(\mathbf{q}) = 0$$

$$-\omega^2 u_{\alpha i}(\mathbf{q}) + \sum_{\beta, j} D_{\alpha i}^{\beta j}(\mathbf{q}) u_{\beta j}(\mathbf{q}) = 0$$

$$\Rightarrow \mathbf{Det}\{D_{\alpha i}^{\beta j}(\mathbf{q}) - \omega^2 \mathbf{1}\} = 0$$

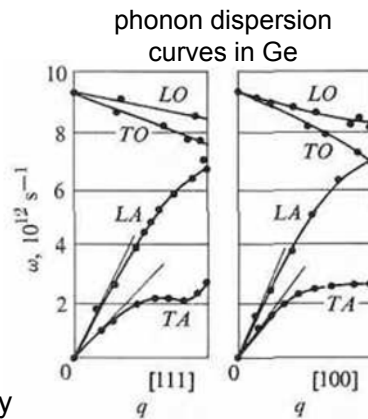
**- dispersion relation**

3s solutions – dispersion branches

3 acoustic, 3s - 3 optical

direction of *u* determines *polarization*  
(longitudinal, transverse or mixed)

Can be degenerate because of symmetry



## Phonons

- Quantum mechanics: energy levels of the harmonic oscillator are quantized
- Similarly the energy levels of lattice vibrations are quantized.
- The quantum of vibration is called a *phonon*  
(in analogy with the photon - the quantum of the electromagnetic wave)

Allowed energy levels of the harmonic oscillator:  $E = (n + 1/2)\hbar\omega$

where  $n$  is the quantum number

A normal vibration mode of frequency  $\omega$  is given by  $\mathbf{u} = \mathbf{A}e^{i(\mathbf{q}\cdot\mathbf{r}-\omega t)}$

mode is occupied by  $n$  phonons of energy  $\hbar\omega$ ; momentum  $\mathbf{p} = \hbar\mathbf{q}$

Number of phonons is given by Planck function:  
( $T$  - temperature) 
$$n = \frac{1}{e^{\hbar\omega/kT} - 1}$$

The total vibrational energy of the crystal is the sum of the energies of the individual phonons:

( $p$  denotes particular phonon branch)

$$E = \sum_{\mathbf{q}^p} E_{\mathbf{q}^p} = \sum_{\mathbf{q}^p} (n_{\mathbf{q}^p} + 1/2)\hbar\omega_p(\mathbf{q})$$

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## Phonon Momentum

- You might think that these phonons have momentum which is  $p = \hbar K$ , just like photons have momentum  $p = E/c$ .
- Be careful! Phonons don't carry momentum like photons do. They can interact with particles like they have a momentum (for example, a neutron can hit a crystal, and start a wave by transferring momentum to the lattice).
- However, you have to think of this momentum as being transferred to the whole lattice. The atoms themselves are not being translated permanently from their equilibrium positions.
- The only exception to this rule is the  $K = 0$  mode, where the whole lattice translates. This, of course, carries momentum.

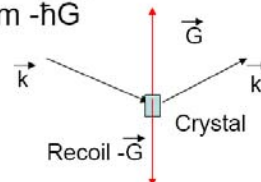
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# Phonon Momentum

- For all practical purposes, a phonon acts as if it carries a momentum  $p = \hbar K$ , which is sometimes called the crystal momentum.
- We have already seen examples of where this is used. For example, if an x-ray interacts with a lattice, then we know that the scattered ray ( $\vec{k}'$ ) and incident ray ( $\vec{k}$ ) have to be related by:

$$\vec{k}' = \vec{k} + \vec{G}$$

- Where  $\vec{G}$  is a reciprocal lattice vector. In this process, the whole crystal recoils with momentum  $-\hbar\vec{G}$



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# Phonon Momentum

- If this photon interacts inelastically with the lattice, then we have:

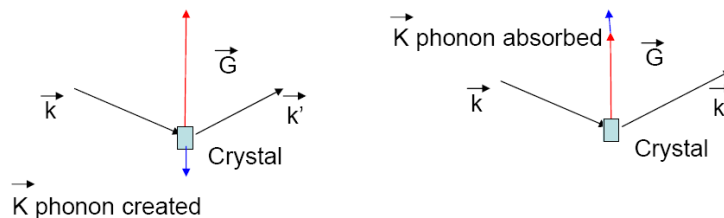
$$\vec{k}' + \vec{K} = \vec{k} + \vec{G}$$

(phonon is created)

- Or:

$$\vec{k}' = \vec{k} + \vec{K} + \vec{G}$$

(phonon is absorbed)



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### Density of states

Consider 1D longitudinal waves. Atomic displacements are given by:

$$u = Ae^{iqx}$$

Boundary conditions: external constraints applied to the ends

Periodic boundary condition:  $u(x=0) = u(x=L)$

Then  $e^{iqL} = 1 \Rightarrow$  condition on the admissible values of  $q$ :

$$q = \frac{2\pi}{L}n \quad \text{where } n = 0, \pm 1, \pm 2, \dots$$

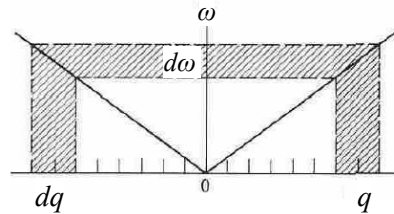
regularly spaced points, spacing  $2\pi/L$

Number of modes in the interval  $dq$  in  $q$ -space :  $\frac{L}{2\pi}dq$

Number of modes in the frequency range  $(\omega, \omega + d\omega)$ :  $D(\omega)d\omega = \frac{L}{2\pi}dq$

$D(\omega)$  - **density of states**

determined by dispersion  $\omega = \omega(q)$



$$D(\omega) = \frac{L}{\pi} \frac{1}{d\omega/dq} \quad 47$$

### Density of states in 3D case

Now have  $\mathbf{u} = \mathbf{A}e^{i(q_x x + q_y y + q_z z)}$

Periodic boundary condition:  $e^{iq_x L} = e^{iq_y L} = e^{iq_z L} = 1$

$$\Rightarrow (q_x, q_y, q_z) = \left( l \frac{2\pi}{L}, m \frac{2\pi}{L}, n \frac{2\pi}{L} \right) \quad l, m, n - \text{integers}$$

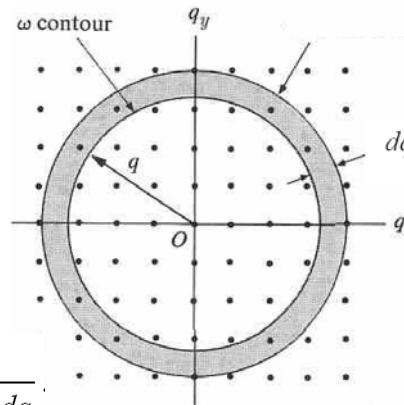
Plot these values in a  $q$ -space, obtain a 3D cubic mesh

number of modes in the spherical shell between the radii  $q$  and  $q + dq$ :

$$\left( \frac{L}{2\pi} \right)^3 4\pi q^2 dq = \frac{V}{(2\pi)^3} 4\pi q^2 dq$$

$V = L^3$  - volume of the sample

$$\Rightarrow \text{Density of states } D(\omega) = \frac{Vq^2}{2\pi^2} \frac{1}{d\omega/dq}$$





### Few notes:

- Equation we obtained is valid only for an *isotropic solid*, (vibrational frequency does not depend on the direction of  $\mathbf{q}$ )
- We have associated a single mode with each value of  $\mathbf{q}$ . This is not quite true for the 3D case: for each  $\mathbf{q}$  there are 3 different modes, one longitudinal and two transverse.
- In the case of lattice with basis the number of modes is  $3s$ , where  $s$  is the number of non-equivalent atoms. They have different dispersion relations. This should be taken into account by index  $p = 1 \dots 3s$  in the density of states.

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### Lattice specific heat (heat capacity)

Defined as (per mole)  $C = \frac{dQ}{dT}$  If constant volume  $V$   $C_V = \left( \frac{\partial E}{\partial T} \right)_V$

The total energy of the phonons at temperature  $T$  in a crystal:

$$E = \sum_{\mathbf{q}, p} \langle n_{\mathbf{q}p} \rangle \hbar \omega_p(\mathbf{q}) = 0 \quad (\text{the zero-point energy is chosen as the origin of the energy}).$$

$$\langle n \rangle = \frac{1}{e^{\hbar\omega/kT} - 1} \quad \text{- Planck distribution} \quad \text{Then} \quad E = \sum_{\mathbf{q}p} \frac{\hbar \omega_p(\mathbf{q})}{e^{\hbar\omega_p(\mathbf{q})/k_B T} - 1}$$

replace the summation over  $\mathbf{q}$  by an integral over frequency:

$$E = \sum_p \int d\omega D_p(\omega) \frac{\hbar \omega}{e^{\hbar\omega/k_B T} - 1}$$

Then the lattice heat capacity is:

$$C_V = \frac{\partial E}{\partial T} = k_B \sum_p \int d\omega D_p(\omega) \frac{\left( \frac{\hbar \omega}{k_B T} \right)^2 e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2}$$

Central problem is to find the density of states

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## Debye model

- assumes that the acoustic modes give the dominant contribution to the heat capacity
- Within the Debye approximation the velocity of sound is taken a constant independent of polarization (as in a classical elastic continuum)

The dispersion relation:  $\omega = vq$ ,  $v$  is the velocity of sound.

In this approximation the density of states is given by:

$$D(\omega) = \frac{Vq^2}{2\pi^2} \frac{1}{d\omega/dq} = \frac{Vq^2}{2\pi^2} \frac{1}{v} = \frac{V\omega^2}{2\pi^2 v^3}$$

Need to know the limits of integration over  $\omega$ . The lower limit is 0.

How about the upper limit? Assume  $N$  unit cells is the crystal, only one atom in per cell  $\Rightarrow$  the total number of phonon modes is  $3N \Rightarrow$

$$\sum_p \int_0^{\omega_D} D(\omega) d\omega = 3N \Rightarrow \omega_D = \left( \frac{6\pi^2 v^3 N}{V} \right)^{1/3} = v(6\pi^2 n)^{1/3} \quad \text{Debye frequency}$$

The cutoff wave vector which corresponds to this frequency is

$$q_D = \frac{\omega_D}{v} = \left( \frac{6\pi^2 N}{V} \right)^{1/3} \quad \text{modes of wave vector larger than } q_D \text{ are not allowed - number of modes with } q \leq q_D \text{ exhausts the number of degrees of freedom}$$

Then the thermal energy is

$$E = 3 \int_0^{\omega_D} d\omega \frac{V\omega^2}{2\pi^2 v^3} \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1}$$

where is "3" from ?

$$\rightarrow E = \frac{3V\hbar}{2\pi^2 v^3} \int_0^{\omega_D} d\omega \frac{\omega^3}{e^{\hbar\omega/k_B T} - 1} = \frac{3Vk_B^4 T^4}{2\pi^2 v^3 \hbar^3} \int_0^{x_D} dx \frac{x^3}{e^x - 1}$$

where  $x \equiv \hbar\omega/k_B T$  and  $x_D \equiv \hbar\omega_D/k_B T \equiv \theta_D/T$

**Debye temperature:**

$$\theta_D = \frac{\hbar v}{k_B} \left( \frac{6\pi^2 N}{V} \right)^{1/3}$$

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The total phonon energy is then  $E = 9Nk_B T \left(\frac{T}{\theta_D}\right)^3 \int_0^{x_D} dx \frac{x^3}{e^x - 1}$

where  $N$  is the number of atoms in the crystal and  $x_D \equiv \theta_D/T$

To find heat capacity, differentiate

$$E = \frac{3V\hbar}{2\pi^2 v^3} \int_0^{\omega_D} d\omega \frac{\omega^3}{e^{\hbar\omega/k_B T} - 1}$$

So,

$$C_V = \frac{3V\hbar^2}{2\pi^2 v^3 k_B T^2} \int_0^{\omega_D} d\omega \frac{\omega^4 e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2} = 9Nk_B \left(\frac{T}{\theta_D}\right)^3 \int_0^{x_D} dx \frac{x^4 e^x}{(e^x - 1)^2}$$

In the limit  $T \gg \theta_D$ ,  $x \ll 1$ ,  $\Rightarrow C_V = 3Nk_B$  - *Dulong-Petit law*

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Opposite limit,  $T \ll \theta_D$ : let the upper limit in the integral  $x_D \rightarrow \infty$

Get

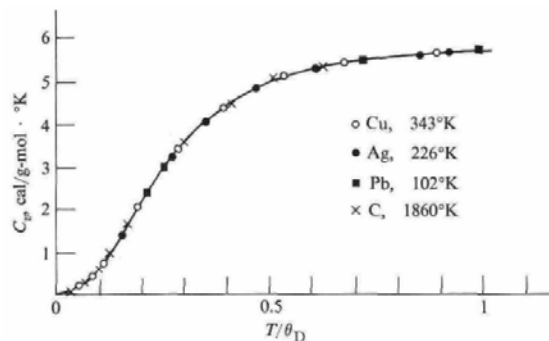
$$E = 9Nk_B T \left(\frac{T}{\theta_D}\right)^3 \int_0^{\infty} dx \frac{x^3}{e^x - 1} = 9Nk_B T \left(\frac{T}{\theta_D}\right)^3 \frac{\pi^4}{15} = \frac{3\pi^4}{5} Nk_B T \left(\frac{T}{\theta_D}\right)^3$$

$$\Rightarrow C_V = \frac{12\pi^4}{5} Nk_B \left(\frac{T}{\theta_D}\right)^3$$

within the Debye model at low temperatures  $C_V \propto T^3$

The Debye temperature is normally determined by fitting experimental data.

Curve  $C_V(T/\theta)$  is *universal* – it is the same for different substances



### Einstein model

The density of states is approximated by a  $\delta$ -function at some  $\omega_E$  :

$$D(E) = N\delta(\omega - \omega_E) \quad \text{where } N \text{ is the total number of atoms -}$$

simple model for optical phonons

Then the thermal energy is 
$$E = \frac{3N\hbar\omega_E}{e^{\hbar\omega_E/k_B T} - 1}$$

The heat capacity is then

$$C_V = \frac{\partial E}{\partial T} = 3Nk_B \left( \frac{\hbar\omega_E}{k_B T} \right)^2 \frac{e^{\hbar\omega_E/k_B T}}{(e^{\hbar\omega_E/k_B T} - 1)^2}$$

The high temperature limit is the same as that for the Debye model:

$$C_V = 3Nk_B \quad \text{- the Dulong-Petit law}$$

At low temperatures  $C_V \sim e^{-\hbar\omega/k_B T}$  - different from Debye  $T^3$  law

Reason: at low T acoustic phonons are much more populated  $\Rightarrow$  the Debye model is much better approximation than the Einstein model

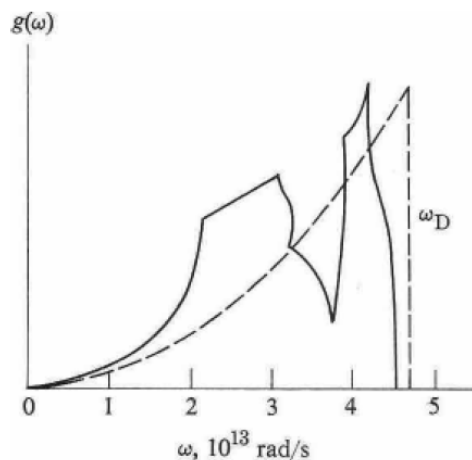
Real density of vibrational states is much more complicated than those described by the Debye and Einstein models.

This density of states must be taken into account in order to obtain quantitative description of experimental data.

The density of states for Cu.

The dashed line is the Debye approximation.

The Einstein approximation would give a delta peak at some frequency.



### Summary

- ❖ In three-dimensional lattice with  $s$  atoms per unit cell there are  $3s$  phonon branches: 3 acoustic,  $3s - 3$  optical
- ❖ **Phonon** - the quantum of lattice vibration.  
Energy  $\hbar\omega$ ; momentum  $\hbar\mathbf{q}$
- ❖ **Density of states** is important characteristic of lattice vibrations;  
It is related to the dispersion  $\omega = \omega(q)$ .  
Simplest case of isotropic solid, for one branch:  $D(\omega) = \frac{Vq^2}{2\pi^2} \frac{1}{d\omega/dq}$
- ❖ Heat capacity is related to the density of states.
- ❖ Debye model – good when acoustic phonon contribution dominates.  
At low temperatures gives  $C_v \propto T^3$
- ❖ Einstein model - simple model for optical phonons ( $\omega(q)$  is constant)
- ❖ At high T both models lead to the Dulong-Petit law:  $C_v = 3Nk_B$
- ❖ Real density of vibrational states is more complicated

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